LEATHER FIBER LUBRICANT RESISTANT TO REMOVAL BY DRY-CLEANING SOLVENTS. II. A RE-EVALUATION BASED ON A NEW ANALYTICAL PROCEDURE FOR *N*-FATTY AMINO ACID IN LEATHER

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ABSTRACT

This report re-evaluates the use of Deriphat 151C†‡, *N*-fatty amino acid ($RNHCH_2CH_2COOH$) (1), as a leather fiber lubricant that is resistant to removal by common dry-cleaning agents — Stoddard solvent, perchloroethylene, and 1,1,2-trichloro-1,2,2-trifluoroethane. It describes also an analytical procedure for this lubricant in leather samples. Data obtained by this new and improved analytical procedure indicate the lubricant to be much more resistant to dry-cleaning solvents than reported previously (2).

INTRODUCTION

In a recent paper (2) we described the use of Deriphat 151C as a leather fiber lubricant in place of fat liquor in garment suede, and presented data to indicate resistance to removal by dry-cleaning solvents. The extraction data for the suede treated with this lubricant were compared to those for suede leathers made with the typical fat liquors used by several tanners. The data published for the samples were obtained by the ALCA Method (Provisional) (3), using chloroform in a Soxhlet extraction apparatus, and were reported on a moisture-free basis. The data indicated that the dry-cleaning loss of the usual fiber lubricants was two to three times greater than the loss of the long chain *N*-fatty amino acid.

Since that publication (2) has appeared, a more detailed study of suedes lubricated with the *N*-fatty amino acid has shown that chloroform is not satisfactory as an analytical solvent for this fiber lubricant. This seems to be true in spite

*Eastern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture.

†Trade name — General Mills.

‡Reference to brand or firm name does not constitute an endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

of the fact that the dry *N*-fatty amino acid, prepared from the commercial solution, is at least 20 percent soluble in chloroform at room temperature.

After some preliminary work with isopropyl and ethyl alcohols, a simple Soxhlet extraction procedure using 95 percent ethyl alcohol was found to be suitable for the analysis of the Deriphat 151C present in leathers.

EXPERIMENTAL

Skins

The New Zealand lambskins used in this study were obtained from a garment suede tanner after they were degreased, chrome-tanned, and retanned with wattle extract. The tanner's degreasing step with a distillate similar to Stoddard solvent lowered the average fat content of the skins to below three percent. The skins were removed from the tanning drum by the tanner just prior to the fat-liquoring step of his process and they were sent to our Laboratory.

Two commercial pieces of suede leather were included in the test. Both contained Deriphat 151C as the fiber lubricant. In addition, one piece was treated with "Quilon"** and the other with "Pentel"†† as water repellents. The feel, nap, and handle of both pieces were very good and commercially acceptable.

Retannage with Glutaraldehyde

The unfinished skins used in these tests were all retanned for 4.5 hours using glutaraldehyde (25 percent concentration) in the amount of ten percent of the wrung weight of the skins, in a 100 percent float, at pH 3.8 to 4.0, and at the temperature range 48 to 53°C. (4,5). The skins were then washed in running water to remove unused glutaraldehyde, wrung, packed in polyethylene bags, and refrigerated to await further processing.

Removal of Natural Fat and Other Soluble Materials from Tanned Skins

To produce a supply of leather substrate for treatment and subsequent analysis by extraction, the experimental skins were cut and pre-extracted as follows. The skins were cut into 5 x 10 in. pieces, the longer dimension at right angles to the backbone. The flanks and ends were discarded. These pieces were spread in a large, shallow pan and immersed in acetone under cover. From time to time, the pieces of skin were moved about in the pan to insure even dilution of the acetone. During a period of about 36 hours, the acetone was drained and replaced three or four times. The extracted pieces were then removed, covered with dish towels, and allowed to air-dry slowly in the laboratory hood. Each dry piece of leather was coiled loosely and extracted in a Soxhlet apparatus as follows:

(a) six hours with chloroform, then air-dried in the hood and followed by

(b) six hours with 95 percent ethyl alcohol, and then air-dried in the hood.

The leather pieces, thus prepared, were the basic samples upon which most of the tests were run, after they were dried in a vacuum oven at 50°C. at about five to ten mm. Hg for 48 hours. The moisture-free weight of each piece was recorded for use in future calculations.

Lubrication of Test Pieces with Deriphat 151C

The test pieces were wet back thoroughly, passed through a wringer, and weighed. The leather pieces were then tumbled in jars containing 15 percent Deriphat 151C dissolved in 50 percent water, both based on the wrung weight of the leather, and two drops of diluted Dow Corning antifoam Reagent "B." The jars were tumbled for one hour and rolled for 30 minutes to insure sufficient agitation. The pieces were removed from the jars and air-dried overnight. Then they were placed in the vacuum oven, as before, for 48 hours at 50°C. After removal from the oven and cooling in a desiccator, the weight of each piece was recorded again. This weight, minus the one previously recorded before treatment, indicated the Deriphat 151C pick-up for each test piece on a moisture-free basis.

Dry-Cleaning Tests

Each 5 x 10 in. piece of leather was cut into two 5 x 5 in. pieces. One piece of each set was put aside for analysis and the data recorded under "before dry-cleaning" (Table III). The other piece of each set was prepared for dry-cleaning. It was stapled to a towel, which helped make up the standard load for the scheduled treatment.

One group of samples was cleaned by the National Institute of Dry-Cleaning (Silver Spring, Maryland) in Stoddard solvent (mineral spirits), so that one sample was cleaned once, another was cleaned twice, and the third sample was cleaned three times. They repeated this routine on another group of samples using perchloroethylene. A similar series was run on samples by the DuPont Dry-Cleaning Products Laboratory using their "Valclene" (1,1,2-trichloro-1,2,2-trifluoroethane) in a "coin-op" machine. The dry-cleaning treatments on these samples were the same, essentially, as those described in more detail in our previous publication (2). When these samples were returned to our Laboratory they were prepared for analysis. The data are recorded under "after dry-cleaning" in Table III.

Analysis

The leather pieces to be analyzed were cut into strips about one fourth to three eighths inch wide. These thin garment suede leathers were cut easily with a paper-trimmer blade. The strips were then cut into small pieces suitable for grinding in a small Wiley Mill fitted with a No. 10 mesh screen. All analyses were run on duplicate portions of the ground sample. Moisture determinations were made on samples dried under vacuum as described previously. Extraction

of the Deriphat 151 C (*N*-fatty amino acid) was done by a procedure essentially similar to the ALCA determination for extractable fat, with the following changes:

(a) Ninety-five percent ethyl alcohol was used in place of chloroform.

(b) The extraction time was 14 hours (two seven-hour periods).

(c) After the solvent was evaporated on a steam bath, the material was dried in a vacuum oven at 50°C. (at five to ten mm. Hg) for 16 hours. This allowed the Deriphat residue to be dried at a moderate temperature.

DISCUSSION AND CONCLUSIONS

The inability to obtain a good analytical material balance on Deriphat 151C in suede leather, using the ALCA analytical method (3), appears to be due to use of chloroform as the analytical solvent. Unpredictably, it is a poor solvent for this *N*-fatty amino acid when present in leather. Our effort to develop an improved analysis for this material, in place of the ALCA Method (Provisional), was redoubled after we were consulted by workers in another laboratory interested in commercial application. They reported difficulty in achieving a nominal material balance in tests on treated suedes of known natural fat content (6). As a result of some preliminary work in our Laboratory, as mentioned in the Introduction, a Soxhlet extraction procedure using 95 percent ethyl alcohol was found to be suitable, although not absolutely quantitative. Tables I and II show values for Deriphat 151C in the leather, determined by actual gain in weight. The percent recovery of this material by extraction is shown also. This recovery range, for 14 hours of extraction, is from 95 to over 99 percent. On the basis of data in Table I, 14 hours was selected as the extraction time; the *N*-fatty amino acid recovery from the samples was increased by seven to ten percent over that obtained in the seven-hour extractions. Recovery data in Table II, on samples containing greater amounts of Deriphat 151C, are in good agreement with the data shown in Table I.

TABLE I

EXTRACTION OF FATTY AMINO ACID (DERIPHAT 151C) FROM LEATHER WITH 95% ETHYL ALCOHOL
EFFECT OF TIME

Sample	Time (Hrs.)	Fatty Amino Acid (%)		
		In Leather*	Extracted	Recovery
1	7	9.36	8.45	90.3
	14		9.09	97.1
2	7	8.39	7.52	89.6
	14		8.35	99.5

*Calculated from gain in weight of treated samples (see Experimental).

TABLE II

COMPARISON OF FATTY AMINO ACID EXTRACTED BY 95% ETHYL ALCOHOL (14 HRS.) AND BY CHLOROFORM (ALCA METHOD)*

	Percent	
	Sample A	Sample B
(a) Fatty Amino Acid (Deriphat 151C) in Sample†	11.3	12.1
(b) Extracted by 95% Ethyl Alcohol (14 Hrs.)	10.8	11.8
(c) Extracted by Chloroform (ALCA Method)‡	5.0	5.6
Recovery of Lubricant with:		
Ethyl Alcohol	95.3	96.4
Chloroform	43.9	46.2

*All analyses run in duplicate, calculated on a moisture-free basis.
†Calculated from gain in weight of treated sample (see Experimental).
‡Extraction for additional six hours will increase values shown by about 0.5.

To show the difference between extraction of Deriphat 151C by 95 percent ethyl alcohol and chloroform from pre-extracted suede treated with Deriphat 151C, a test was run on two leather samples, A and B, as listed in Table II. Ground leather from each sample was extracted with 95 percent ethyl alcohol for 14 hours (see Experimental). Other portions of ground leather from each sample were extracted with chloroform according to the ALCA Method. The data in Table II show that the ethyl alcohol removes well over 95 percent of the lubricant applied, whereas chloroform extraction removes much less than 50 percent of the lubricant applied. This poor showing by chloroform would not ordinarily be expected, considering the appreciable solubility of dry Deriphat 151C in chloroform.

As a result of the incomplete removal of the lubricant by chloroform extraction, the data shown in our previous publication (2) do not reflect an accurate picture of the quantity of Deriphat in the samples and the actual effects of the several dry-cleaning agents thereon. To clarify the effect of dry-cleaning, samples of suede were prepared and cleaned as described under Experimental. The data are recorded in Table III. It is of special interest to note that, when a fairly accurate means of analysis is available, there appears to be essentially no loss of fiber lubricant due to any of the three dry-cleaning solvents tested. This is to be compared with the appreciable losses reported previously (2). In fact, many of the samples show a slightly higher extractable content after dry-cleaning than before. This is because the lubricant content of experimental skin samples, cut from neighboring locations, can vary by one percent or more.

In the case of the tests on Deriphat 151C-treated "commercial" samples listed in Table III, the loss (Δ) shown by dry-cleaned pieces is due to the natural fat in the skins, which is also extracted during the analysis.

TABLE III

EFFECT OF DRY-CLEANING ON ETHYL ALCOHOL EXTRACTABLES* FROM EXPERIMENTAL AND COMMERCIAL SUEDE LEATHERS TREATED WITH *N*-FATTY AMINO ACID FIBER LUBRICANT†

Dry-Cleaning Solvents, Cleaning Cycles	% Extractable with 95% Ethyl Alcohol‡		
	Before Dry-Cleaning	After Dry-Cleaning	
	Experimental Suede		
Valclene††			
1 cycle(s)	9.5	9.9	
2 "	11.3	11.0	
3 "	10.1	10.5	
Perchloroethylene			
1 cycle(s)	11.5	11.5	
2 "	11.8	10.7	
3 "	10.1	11.0	
Stoddard			
1 cycle(s)	9.6	10.3	
2 "	10.8	9.8	
3 "	9.0	10.1	
	Commercial Suede**		
Valclene††			
			Δ‡‡
1 cycle(s)	8.6	6.4	−2.2
2 "	9.7	7.1	−2.6
Stoddard			
1 cycle(s)	8.6	6.1	−2.5
2 "	9.7	6.5	−3.2

*Soxhlet extraction — 14 hours.

†Deriphat 151C (see Reference 2).

‡All analyses were run in duplicate, calculated on a moisture-free basis.

**Deriphat 151C used in tannery as leather lubricant in place of standard fatliquor; sample skins from a pilot-scale lot made and sold.

††A DuPont commercial dry-cleaning agent (1,1,2-trichloro-1,2,2-trifluoroethane).

‡‡This difference is due mainly to loss of natural fat in commercial product.

The degree of accuracy achieved by extractive analysis of fats, etc., from leather has been a matter of study for many years. The ALCA method already mentioned has been listed as "Provisional" since 1957 with an active committee still interested in improvements and revision. The Method has no precision statement. The British Method (7) using dichloromethane requires duplicate determinations to vary from one another by no more than 0.2 percent, calculated on the original weight of the leather. As far as quantitative recovery is concerned, the following statement in this method is significant and applies to the

subject of this report as well: "All fatty and similar substances cannot be extracted from leather with organic solvents — they may be in part soluble and partly bound in leather."

Duplicate analyses using 95 percent ethyl alcohol on 28 samples containing Deriphat 151C gave: 20 sets within 0.2 percent; five sets checked within 0.3 percent; three sets varied within 0.4 percent.

REFERENCES

1. Deriphat 151C. Technical Bulletin 15A (1961), Chem. Div., General Mills, Inc., 4620 W. 77th Street, Minneapolis, Minnesota 55435.
2. Fein, M. L., Viola, S. J., Filachione, E. M., and Naghski, J. *JALCA,* **65**, 5 (1970). Presented in part at ALCA Meeting, Bretton Woods, N. H., June, 1968.
3. Provisional Method B4 (1957). Official Method of Analysis, ALCA. May be obtained from Secretary-Treasurer of ALCA, Tanners' Council Research Laboratory, University of Cincinnati, Cincinnati, Ohio 45221.
4. Fein, M. L., Filachione, E. M., Naghski, J., and Harris, E. H., Jr., *JALCA,* **58**, 202 (1963).
5. Filachione, E. M., Fein, M. L., and Harris, E. H., Jr. *JALCA,* **59**, 281 (1964).
6. Private Communication.
7. Method SLC 4:1966 (I.U.C./4). Official Method of Analysis (Society of Leather Trades' Chemists), 4th Revised Ed., 52 Crouch Hall Lane, Redbourn, Herts, England.